Final Report: NASA TRACE-P Proposal & Two Letter Proposal Extensions for One Additional Year

"Airborne Measurements of Formaldehyde Employing a Tunable Diode Laser Absorption Spectrometer During TRACE-P"

Original Project Duration:
July 1, 2000 – June 30, 2002

Letter Proposal Extensions:
July 1, 2002 – Sept. 30, 2002
Oct. 1, 2002 – June 30, 2003

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Introduction

This final report summarizes the progress achieved over the entire 3-year proposal period including two extensions spanning 1 year. These activities include: 1) preparation for and participation in the NASA 2001 TRACE-P campaign using our airborne tunable diode laser system to acquire measurements of formaldehyde (CH_2O); 2) comprehensive data analysis and data submittal to the NASA archive; 3) follow up data interpretation working with NASA modelers to place our ambient CH_2O measurements into a broader photochemical context; 4) publication of numerous JGR papers using this data; 5) extensive follow up laboratory tests on the selectivity and efficiency of our CH_2O scrubbing system; and 6) an extensive follow up effort to assess and study the mechanical stability of our entire optical system, particularly the multipass absorption cell, with aircraft changes in cabin pressure.

The results of the first four activities are summarized in the following JGR publications:

1. Wert, B.P., **A. Fried**, S. Rauenbuehler, J. Walega, and B. Henry, *Design and Performance of a Tunable Diode Laser Absorption Spectrometer for Airborne Formaldehyde Measurements.* J. Geophys. Res., **108**, (D12), doi: 10.1029/2002JD002872, 2003.

2. **Fried, A.**, J. Crawford, J. Olson, J. Walega, W. Potter, B.P. Wert, C. Jordon, B. Anderson, R. Shetter, B. Lefer, D. Blake, N. Blake, S. Meinardi, B. Heikes, D. O'Sullivan, J. Snow, H. Fuelberg, C.M. Kiley, S. Sandholm, D. Tan, G. Sachse, H. Singh, I. Faloona, C.N. Harward, and G.R. Carmichael, *Airborne Tunable Diode Laser Measurements of Formaldehyde During TRACE-P: Distributions and Box-Model Comparisons*, J. Geophys. Res., **108** (D20), 8798, doi: 1029/2003/JD003451, 2003.

3. Olson, J.R, J. Crawford, G. Chen, **A. Fried,** M. Evans, C. Jordon, S. Sandholm, D. Davis, B. Anderson, M. Avery, J. Barrick, D. Blake, W. Brune, F. Eisele, F. Flocke, H. Harder, D. Jacob, Y. Kondo, B. Lefer, M. Martinez, R. Mauldin, G. Sachse, R. Shetter, H. Singh, R. Talbot, and D. Tan, T*esting Fast Photochemical Theory During TRACE-P Based on Measurements of OH, HO_2, and CH_2O*, J. Geophys. Res., **109 (D15),** S10, doi: 10.1029/2003JD004278.

4. Browell, E.V., M.A. Fenn, C.F. Butler, W.B. Grant, V.G. Brackett, J.W. Hair, M.A. Avery, R.E. Newell, Y. Hu, H.E. Fuelberg, D.J. Jacob, B.E. Anderson, E.L. Atlas, D.R. Blake, W.H. Brune, J.E. Dibb, **A. Fried**, B.G. Heikes, G.W. Sachse, S.T. Sandholm, H.B. Singh, R.W. Talbot, S.A. Vay, and R.J. Weber, *Large-Scale Ozone and Aerosol Distributions, Air Mass Characteristics, and Ozone Fluxes Over the Western Pacific Ocean in Late-Winter/Early Spring,* J. Geophys. Res., **108** (D20), 8805, doi: 10.1029/2002JD003290, 2003

5. Russo, R., R. Talbot, J. Dibb, E. Scheuer, G. Seid, C. Jordan, G. Sachse, M. Avery, S. Vay, D. Blake, N. Blake, E. Atlas, **A. Fried,** S. Sandholm, D. Tan, H. Singh, J. Snow, B. Heikes, and H. Fuelberg, *Chemical Composition of Asian Continental Outflow Over the Western Pacific: Results from TRACE-P,* J. Geophys. Res, **108** (D20), 8804, doi: 10.1029/2002JD003184, 2003.

6. Carmichael, G.R., Y. Tang, G. Kurata, I. Uno, D.G. Streets, N. Thongboonchoo, J-Hun Woo, S. Guttikunda, A. White, T. Wang, D.R. Blake, E. Atlas, **A. Fried,** B. Potter, M.A. Avery, G.W. Sachse, S.T. Sandholm, Y. Kondo, R.W. Talbot, A. Bandy, D. Thorton, and A.D. Clarke, *Evaluating Regional Emission Estimates Using The TRACE-P Observations,* J. Geophys. Res., **108 (D21)**, 8810, doi:10.1029/2002JD003116, 2003.

7. Carmichael, G.R., Y. Tang, G. Kurata, I. Uno, D.G. Streets, J-Hun Woo, H. Huang, J. Yienger, B. Lefer, R.E. Shetter, D.R. Blake, **A. Fried,** E. Apel, F. Eisele, C. Cantrell, M.A. Avery, J.D. Barrick, G.W. Sachse, W. Brune, S.T. Sandholm, Y. Kondo, H.B. Singh, R.W. Talbot, A. Bandy, A.D. Clarke, and B.G. Heikes, *Regional-Scale Chemical Transport Modeling in Support of Intensive Field Experiments: Overview and Analysis of the TRACE-P Observations* **108 (D21)**, 8823, doi:10.1029/2002JD003117, 2003

8. Eisele, F.L., L. Mauldin, C. Cantrell, M. Zondlo, E. Apel, **A. Fried,** J. Walega, R. Shetter, B.Lefer, F. Flocke, A. Weinheimer, M. Avery, S. Vay, G. Sachse, H. B. Singh, W. Brune, H. Harder, M. Martinez, A. Bandy, D. Thornton, B. Heikes, Y. Kondo, D. Riemer, S. Sandholm, D. Tan, R. Talbot, and Jack Dibb, *Summary of Measurement Intercomparisons During TRACE-P*, J. Geophys. Res., **108** (D20), 8791, doi: 10.1029/2002JD003167, 2003.

9. Cantrell, C.A., G.D. Edwards, S. Stephens, R.L. Mauldin, M. Zondlo, E. Kosciuch, F.L. Eisele, R.E. Shetter, B.L. Lefer, S. Hall, F. Flocke, A. Weinheimer, **A. Fried,** E. Apel, Y. Kondo, D.R. Blake, N. Blake, I. Simpson, A. Bandy, D. Thornton, B. Heikes, H. Singh, W. Brune, H. Harder, M. Martinez-Harder, M.A. Avery, S. Vay, J.D. Barrick, G.W. Sachse,J.R. Olson, and J.H. Crawford, *Peroxyl Radical Behavior During TRACE-P as Measured Aboard the NASA P-3B Aircraft,* J. Geophys. Res., **108** **(D20)**, 8797, doi:10.1029/2003JD003674, 2003.

10. Singh, H.B., L.J. Salas, R.B. Chatfield, E. Czech, **A. Fried,** J. Walega, M. Evans, B. Fields, D.J. Jacob, D. Blake, B. Heikes, R. Talbot, G. Sachse, J. Crawford, M. Avery, S. Sandholm, and H. Fuelberg, *Analysis of the Atmospheric Distribution, Sources, and Sinks of Oxygenated Organic Chemicals Based on Measurements Over the Pacific During TRACE-P*, J. Geophys. Res., in press 2003

In task #5, an extensive follow up set of laboratory tests were carried out on the selectivity and efficiency of our airborne CH_2O scrubbing system. This scrubbing system consists of a heated Pd/Al_2O_3 catalyst through which a controlled flow of compressed ambient air is passed and redirected, as required, to the entrance of our aircraft inlet system. The scrubbed air was not further dried. An extensive set of tests was originally carried out on this scrubbing system. However, as discussed in the letter proposal requesting augmentation funding, at very low ambient CH_2O mixing ratios around 50 parts-per-trillion (pptv) and less, the performance of this scrubbing system becomes more and more critical to the overall accuracy of the retrieved CH_2O results. This and the fact that our detection limits have significantly improved since the original tests warranted a revisit of systematic studies of the scrubber system. These tests involved a careful re-assessment of scrubbing efficiency using different input relative humidities, and a combination of various scrubber temperatures, pressures and flow rates.

Variable measured H_2O mixing ratios were added to the scrubber inlet using a H_2O saturator and a dew point hygrometer. At typical scrubber operational temperatures around 300 °C, the addition of H_2O vapor to the scrubber was found to produce a small but persistent positive interference in the acquired background spectra. Although subsequent tests eliminated the possibility that residual CH_2O scrubber breakthrough was the cause, we were not able to further determine if H_2O in the scrubber resulted in secondary photochemistry, producing a scrubber artifact that is detected as CH_2O. Clearly further work will be devoted to finding the exact cause of this artifact in the future. However, the present tests indicate that during TRACE-P our retrieved CH_2O

mixing ratios in the boundary layer may be too low by approximately 90 pptv, which when compared to typical mixing ratios above 1 ppbv, makes this potential error unimportant. At high altitudes above 30,000 feet the retrieved CH_2O mixing ratios may be too low by 0 to 40 pptv. No corrections to the TRACE-P data were made since the actual H_2O reaching the scrubber during this mission was not measured. Fortunately these errors are small and within our total measurement uncertainty. Nevertheless, it is highly desirable to eliminate this effect in future missions such as the INTEX-NA study, where CH_2O mixing ratios in the upper troposphere can be on the order of the corrections. To address this issue, we employed during INTEX-NA a complete AAdco zero air scrubber system, which includes a molecular sieve drying system before the Pd/Al_2O_3 catalyst, for this purpose. In this case any potential artifact would be less than 10 pptv, well below our limit of detection.

In task #6, extensive follow up studies were carried out to assess the mechanical stability of our entire optical system, particularly the multipass absorption cell, with aircraft changes in cabin pressure. A comprehensive discussion of the findings of this study have been incorporated in the undergraduate diploma thesis of Christoph Dyroff ("Performance Assessment and Design Improvement of a Herriott type Multipass Absorption Cell for highly sensitive Trace-Gas Measurements" A Thesis for partial Fulfillment of the Requirements for the Degree Dipl. Ing. (FH) in the Degree Course Angewandte Lasertechnik, 2003 Fachhochschule Oldenburg/Ostfriesland/Wilhelmshaven -University of Applied Sciences-Emden, Germany, Department of Technology). Mr. Dyroff was a visiting German engineering student who worked in our group and investigated Herriott cell deflections from differential pressures across the cell using various computer analysis tools as well as laboratory measurements. A new Herriott cell with improved performance characteristics resulted from this work, and this effort and the resulting improvements are documented in the poster paper found in the Appendix of this report. Although there was no time to incorporate this particular cell design in the subsequent INTEX-NA measurements, temporary solutions based on these findings were implemented during the INTEX-NA study. In addition, numerous other improvements to further stabilize the optics, which were identified during and after this proposal extension period, were also implemented for the INTEX-NA study. As a result, small performance degrading perturbations to the optical alignment caused by changes in aircraft cabin pressure and aircraft accelerations were greatly minimized during the INTEX-NA study.

APPENDIX

Poster Presentation at the 2004 Conference on Laser Applications to Chemical and Environmental Analysis

Annapolis, Maryland

"Design and performance assessment of a stable astigmatic Herriott cell for trace gas measurements on airborne platforms"

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Abstract: The present paper discusses a new, more stable, astigmatic Herriott cell employing carbon fiber stabilizing rods. Laboratory tests using a near-IR absorption feature of CO at 1564.168-nm revealed a factor of two improvement in measurement stability compared with the present commercial design when the sampling pressure was changed by ± 2 Torr around 50 Torr. This new cell should significantly enhance our efforts to measure trace gases employing pathlengths of 100 to 200-meters on airborne platforms with minimum detectable line center absorbances of less than 10^{-6}.

1. Introduction

Measurement of various gases in the atmosphere at very low trace levels from several to several thousand parts-per-trillion by volume (where 1 pptv is equivalent to a volume mixing ratio of 1×10^{-12}) are important for advancing our understanding of atmospheric chemical transformations and processes. Frequently, such measurements are carried out employing infrared (IR) laser absorption spectroscopy utilizing a multipass absorption cell to redirect the IR beam back and forth many times to increase the measured absorbance, and hence the sensitivity. Absorption cells based upon the designs of White, Herriott or modifications thereof, are typically employed to achieve pathlengths in the 10's of meters to 200-meter range for this purpose. McManus et al. [1] developed and commercialized a modified Herriott cell using astigmatic mirrors to optimize the pathlength to cell volume ratio by more effectively utilizing the entire surface areas of both mirrors. McManus et al. [1] have demonstrated that the position of the output beam is very stable as long as the distance between the mirrors and their angles are not changed by, for example, cell flexure of the end plates or the baseplate. Our extensive field measurements employing such a cell to detect the trace gas formaldehyde (CH_2O) have confirmed such stability, even on airborne platforms where varying conditions of cabin temperature, cabin pressure and aircraft vibrations, severely challenge the measurement. In one such study, Fried et al. [2 and references therein], demonstrated 1-minute detection limits (LOD, 2σ replication precision) for airborne CH_2O measurements, which typically fell within the 50 – 80 pptv range employing a 100-m pathlength absorption cell with a liquid-nitrogen cooled lead-salt diode laser source. On occasion, 2σ detection limits in the 30 – 40 pptv range has been achieved. The above detection limits correspond to minimum detectable line center absorbances within the $1.0 – 2.7 \times 10^{-6}$ range. While this performance is remarkable and sufficient for many atmospheric studies, even higher performance is required for many gases like CH_2O where ambient concentrations attain levels in the 20 – 30 pptv range. In this case it is highly desirable to achieve detection limits a factor of 3 – 6 lower on a routine basis on airborne platforms. The present paper and associated talk will discuss some of the approaches to achieve this end.

As observed by Fried et al. during numerous aircraft campaigns and further quantified by Wert et al. [3], changes in aircraft cabin pressure as small as 11 Torr lead to large changes in background absorption structure, which in turn lead to degradation in measurement performance. Although subtle alignment changes of the many discrete optical components may be partially responsible, preliminary laboratory evidence suggests that most if not all of the change in background absorption structure can be attributed to dynamic flexure of the astigmatic cell baseplate. It is believed that the cell baseplate, stabilizing rod, and ultimately the mirror housings all flex as the cabin pressure is changed due to changes in aircraft altitude. In addition, the cell window may also flex. Since the cell is operated at a constant reduced pressure between 40 and 50 Torr, such cabin pressure changes result in a variable differential pressure across the entire cell structure, which in turn can affect the background structure. Depending upon the magnitude and the phase of these background changes relative to the acquisition sequence, the performance may be severally degraded.

In the present study, a new more stable astigmatic multipass cell has been designed, constructed, and tested to address the pressure-induced cell flexure problem discussed above. The cell design is based upon the fundamental Aerodyne Research, Incorporated astigmatic Herriott cell with the addition of 4 carbon fiber stabilizing rods in place of the cell baseplate and the single thin stabilizing rod. The new cell, which is shown in Figure 1, utilizes dielectric-coated mirrors centered at 3.5µm, to achieve pathlengths of 200-meters.
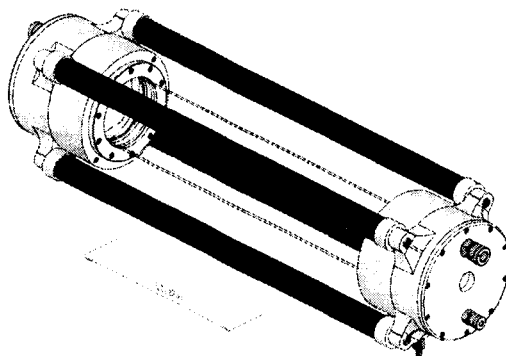
Figure 1: Model of the 200 m multipass cell. The cell is 71 cm long, the sample volume is approximately 4.2 Liters, and the complete cell weighs 11.3 kg.

Numerous tests of the new cell have been carried out in the laboratory, and these will be presented in a future publication. The present paper focuses on the results for one of these studies, a comparison of the measurement precision obtained using the new cell with those from our present airborne Herriott cell as a function of pressure. For the present tests, the sampling pressure in the cell was changed since we could not readily change the ambient pressure. The comparisons were carried out using a near-IR DFB diode laser. This laser was scanned over a weak carbon monoxide (CO) absorption feature 1564.168-nm using a 50-Hz saw-tooth ramp with a 50 kHz triangle modulation simultaneously applied. The modulated signal was captured using a high quality lock-in amplifier, the 2f signal determined and subsequently co-averaged by computer. In a typical measurement sequence, one 10-second background spectrum was recorded by adding zero air (air scrubbed of CO) into the cell inlet, and after a delay period of 7 seconds (4 cell e-folding periods), a 1-minute "ambient sample" was recorded. This was followed by another 7 second flushing period and a second 10-second background acquisition. The two backgrounds were averaged and subtracted point-by-point from the 1-minute "ambient sample". The resultant spectrum was then fit to a previously acquired calibration spectrum, obtained by flowing a 14-ppm CO standard through the cell at a constant pressure of 50 Torr. The "ambient samples" of the present measurements were acquired using zero air, and this procedure allowed us to examine the resulting precision and its degradation as the cell sampling pressure was changed. In an ideal system with no pressure-induced changes, one would expect to retrieve "ambient" values of 0 with a precision governed by the instrument LOD, and these results should be invariant to small changes in sampling pressure. For the present tests, two different types of pressure changes were implemented for both cells. In the first, the pressure was changed by ± 2 Torr during the background acquisition phase only (48 to 52 Torr). All pressure changes were implemented during the 7-second flushing phase before the data was acquired. The pressure during the intervening "ambient sample" phase was kept constant at 50 Torr. In the second test, the pressure was changed by ± 2 Torr during the

"ambient" phase while the background acquisition pressure was fixed at 50 Torr. These tests are designed to simulate various cabin pressure change scenarios. On some occasions one would expect a combination of both results, namely a change in cabin pressure during the ambient and both background acquisition periods.

The results, which are displayed in Fig. 2, show nearly comparable measurement precision for the two cells when the pressure was held constant at 50 Torr during all phases. Likewise, the measurement precision for the new cell when the pressure was changed during the background phase was nearly identical to the constant pressure case. Apparently, pressure changes during the two background phases are self-compensating in the new cell. This is in contrast to the old cell where the precision degraded by a factor of ~ 2. The precisions were degraded in both cells when the pressure was changed during the "ambient" phase. However, the degradation was a factor of ~ 2 worse with the old cell. Additional laboratory measurements strongly suggest that the new cell structure does not flex with changes in pressure, but rather the window flexes. In the old cell, we believe both components flex with changes in pressure. In any event, these tests clearly show an improvement in measurement precision employing the new stabilized cell. Since we ultimately plan to couple a new difference frequency generation (DFG) laser source with the new cell utilizing a pressure-controlled interface, we expect even lower pressure-induced degradation since the cell window will be not experience the changes in pressure encountered during the present tests.
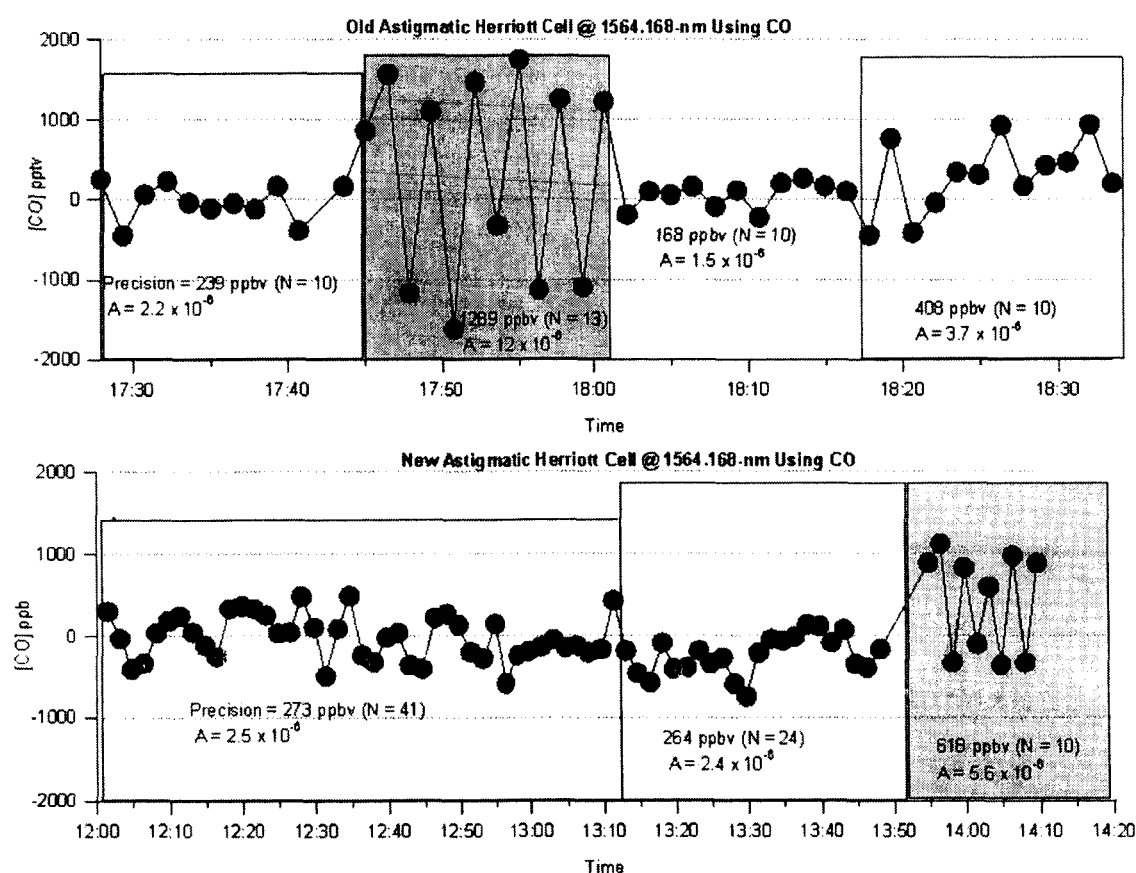
Figure 2: Time series of one-minute averages when changing the cell pressure of the present commercial cell (top trace) versus the new cell (bottom). The non-shaded regions represent constant pressure while the light and dark gray regions represent varying pressure during the background and "ambient" phases, respectively. The 1-minute retrieved (1σ) precisions are given along with the line center absorbances (A) for each measurement sequence.

References:

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3. B.P. Wert, et al., "Design and performance of a tunable diode laser absorption spectrometer for airborne formaldehyde measurements", J. Geophys. Res., **108 (D12),** doi: 10.1029/2002JD002872, 2003.

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